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THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

Valerie JEANNE-ROSE et al.

Application No.: 09/902,660

Filing Date: July 12, 2001

For: USE OF AN ORGANOMETALLIC  
COMPOUND TO PROTECT  
AND/OR STRENGTHEN A  
KERATIN MATERIAL, AND  
TREATMENT PROCESS

Group Art Unit: 1615

Examiner: unassigned

Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

**REQUEST FOR CORRECTED PATENT APPLICATION  
PUBLICATION UNDER 37 C.F.R. § 1.221(b)**

The U.S. Patent and Trademark Office published the above-identified Application No. 09/902,660 as Publication No. US-2002-0041856-A1, on April 11, 2002. The published application contains material mistakes that are the fault of the Office. Attached hereto is a copy of each relevant page of the originally filed application and a marked-up copy of the corresponding page of the published application containing the mistakes.

The mistakes, which are indicated in red ink on the relevant pages of the marked-up copy of the published application attached hereto, are material since they affect the public's ability to appreciate the technical disclosure of the patent application publication or determine the scope of the provisional rights that an applicant may seek to enforce upon issuance of a patent. See C.F.R. § 1.221(b). The mistakes are as

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follows (line numbers refer to lines with text):

On page 3, in paragraph [0055], line 1, the published application reads " $\Sigma$ -N" whereas, it should read " $\epsilon$ -N-". See page 10, line 19 of the originally filed application (copy attached and highlighted for the Office's convenience).

On page 4, in paragraph [0075], line 1, the published application reads "(N—(6-aminohexyl)" whereas, it should read "(N-(6-aminohexyl)". See page 11, line 23 of the originally filed application (copy attached and highlighted for the Office's convenience).

On page 4, in paragraph [0081], the published application reads "methyidiethoxysilane" whereas, it should read "methyldiethoxysilane". See page 12, line 5 of the originally filed application (copy attached and highlighted for the Office's convenience).

On page 4, in paragraph [0082], the published application reads "methyidimethoxysilane" whereas, it should read "methyldimethoxysilane". See page 12, line 6 of the originally filed application (copy attached and highlighted for the Office's convenience).

On page 6, in paragraph [0130], line 8, the published application reads " $k(N/m)$ " whereas, it should read " $K(N/m)$ ". See page 19, line 15 of the originally filed application (copy attached and highlighted for the Office's convenience).

On page 7, in paragraph [0159], line 11, the published application reads " $M-(OR_1)_n(I_a)$ " whereas, it should read " $M-(OR_1)_n$  (I<sub>a</sub>)". See page 24, line 5 of the originally filed application (copy attached and highlighted for the Office's convenience).

On page 8, col. 1, line 40, the published application is illegible and incomplete whereas, it should read "RR'-M-(Z)<sub>n-x-2</sub>(X)<sub>x</sub>". See page 25, line 23 of the originally filed application (copy attached and highlighted for the Office's convenience).

On page 10, in claim 38, line 17, the published application reads "N—(trimethoxysilylpropyl)" whereas, it should read "N-(trimethoxysilylpropyl)". See page 33, line 3 of the originally filed application (copy attached and highlighted for the Office's convenience).

On page 10, in claim 38, lines 29, 30, 34 the published application reads "methyidiethoxysilane" whereas, it should read "methyldiethoxysilane". See page 33 lines 14, 15, and 19 of the originally filed application (copy attached and highlighted for the Office's convenience).

On page 10, in claim 38, line 33, the published application reads "[ (HOCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>O ]<sub>2</sub>Ti(OC<sub>3</sub>H<sub>7</sub>)<sub>2</sub>" whereas, it should read "[ (HOCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>O]<sub>2</sub>Ti(OC<sub>3</sub>H<sub>7</sub>)<sub>2</sub>". See page 33 lines 18 of the originally filed application (copy attached and highlighted for the Office's convenience).

For at least the foregoing reasons, Applicants request that the Office correct the above-identified material mistakes in the published application. Further, Applicants request that the Office forward a copy of the corrected published application or at least a notification of the occurrence or predicted occurrence of the corrected publication once it has been corrected.

Applicants believe that no petition or fee is due in connection with this request. If any Petition or fee is due, please grant the Petition and charge the fee to our Deposit Account No. 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,  
GARRETT & DUNNER, L.L.P.

By: 

Brian M. Burn  
Reg. No. 44,455

Date: June 11, 2002

Enclosures:

- Marked-up copy of the cover page, and pages 3, 4, 6, 7, 8, and 10 of the published application
- Highlighted copy of pages 10, 11, 12, 19, 24, 25, and 33 of the originally filed application.

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branched and cyclic, saturated and unsaturated,  $C_{1-30}$  hydrocarbon-based radicals, such as  $C_{2-20}$  hydrocarbon-based radicals.

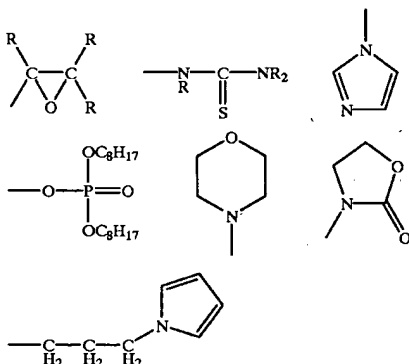
[0040] Among the cosmetically active groups which may be represented and/or borne by  $R$ ,  $R'$ , and  $R''$  and borne by  $X$ , mention may be made of a colorant group; a photochromic group; a group for screening out UV-A and/or UV-B radiation; a group for promoting adhesion to keratin materials, such as an amide, urethane, urea, hydroxyl, carboxyl, amino acid or polypeptide group; a group which facilitates make-up removal; a bacterial or bacteriostatic group; a chelating group, for example, one which can complex multivalent cations; a hydroxy acid; a group for preventing hair loss; an antioxidant group; a free-radical-scavenging group; and a vitamin-bearing group.

[0041] For example, the at least one metallic precursor may be chosen from at least one compound chosen from formulae (Ia), (Ib), (Ic), (Id) and (IIa), and, as a further example, from formulae (Ia), (Ib) and (IIa).

[0042] The metal atom  $M$ , for example, may be chosen from titanium, zirconium, aluminium, iron, tin and silicon and as a further example, from titanium and silicon.

[0043] For example,  $R_1$  may be chosen from linear and branched, saturated hydrocarbon-based radicals containing 1 to 30 carbon atoms, such as, in a further example, from 1 to 6 carbon atoms. As even a further example,  $R_1$  may be chosen from methyl, ethyl, propyl, n-butyl, isobutyl and t-butyl radicals.

[0044] For example,  $R$  and  $R'$ , which may be identical or different, may be chosen from linear or branched, saturated  $C_{1-20}$  hydrocarbon-based radicals, such as  $C_{1-6}$  hydrocarbon-based radicals; or, as a further example, from linear or branched, saturated  $C_{1-20}$  hydrocarbon-based radicals, such as  $C_{1-6}$  hydrocarbon-based radicals, substituted with at least one substituent chosen from a halogen atom (such as perfluorinated),  $-\text{NH}_2$ ,  $-\text{CO}-\text{NH}_2$ ,  $-\text{SH}$ ,  $-\text{CO}_2\text{H}$ ,  $-\text{COR}$ ,  $-\text{OH}$ ,  $-\text{N}=\text{C}=\text{O}$ ,  $-\text{NH}-\text{CO}-\text{NH}_2$ ,  $-\text{N}^+\text{R}_3$ , such as,  $-\text{N}^+\text{Bu}_3$ ,  $-\text{C}(\text{NH}_2)_2$ , benzenesulphonate;



[0045] in which the various radicals  $R$ , which may be identical or different, are chosen from hydrogen and linear, branched and cyclic, saturated or unsaturated,  $C_{1-30}$  hydrocarbon-based radicals, such as  $C_{2-20}$  hydrocarbon-based radicals.

[0046] For example,  $R''$  may be chosen from  $-\text{O}-$ ,  $-\text{NH}-$  and linear and branched, saturated  $C_{1-30}$  divalent hydrocarbon-based radicals, such as  $C_{2-20}$  divalent hydrocarbon-based radicals, optionally interrupted with at least one hetero atom chosen from O, N, P and S.

[0047] For example,  $X$  may be chosen from carboxylic acids, sulphonic acids, phosphonic acids, phosphoric acids, sulphuric acids, ketones,  $\beta$ -diketones, esters,  $\beta$ -keto esters, amines,  $\beta$ -keto amines, amino acids, such as  $\alpha$ - and  $\beta$ -hydroxylated amino acids and derivatives thereof,  $\alpha$ - and  $\beta$ -hydroxylated acids, ethers and polyethers, imines, amides, said amides being optionally hydroxylated, azo compounds, thiols, ureidos, thioether sulphoxides, thioether sulphones, optionally cyclic thioethers, di (thioethers), monoalcohols and polyols, dextrin and its derivatives, thiazolidines; hydrocarbon-based polymers optionally comprising hetero atoms chosen from N, O, S and P, said polymers, being obtained, for example, by free-radical polymerization, by condensation or by controlled "living" polymerization, and said polymers having a (weight-average) molecular weight ranging from 90 to 10 000, such as, for example, from 100 to 1 000, and as a further example from 150 to 500; and derivatives thereof.

[0048] Mention may be made, for example, of:

[0049] salicylic acid and its derivatives such as 4-(meth)acrylaminosalicylic acid and 5-(meth)acrylamido-salicylic acid;

[0050] lactic acid; succinic acid; acetic acid; citric acid;

[0051] acrylic acid esters or methacrylic acid esters, such as acetoxyethyl (meth) acrylate; methyl  $\alpha$ -hydroxy (meth) acrylate;

[0052] ethyl acetoacetate of formula  $\text{CH}_3-\text{CO}-\text{CH}_2-\text{COOCH}_2\text{CH}_3$ , methyl acetoacetate of formula  $\text{CH}_3-\text{CO}-\text{CH}_2-\text{COOCH}_3$  and acetylacetone of formula  $\text{CH}_3-\text{CO}-\text{CH}_2-\text{CO}-\text{CH}_3$ ;

[0053] EDTA;

[0054] low molecular weight polyethers ( $n$  ranging from 1 to 12) such as poly (ethylene glycols) and poly (propylene glycols);

[0055] lysine and its derivatives, such as  $\epsilon$ -N-(meth)acryloyl-L-lysine; lower case epsilon symbol

[0056] cysteine and its derivatives, such as N-acetyl-cysteine, N-acetylcysteine disulphides and carboxymethylcysteine;

[0057] cystine; methionine;

[0058] lactic acid esters or acetic acid esters

[0059] triethanolamine;

[0060] cysteine and its derivatives;

[0061] lipoic acids;

[0062] dextrin and cyclodextrin;

[0063] polymers of polyethylene glycol, polypropylene glycol or polyethylenimine type; and

[0064] diketones such as 2, 4-pentanedione, 2, 4-hexafluoropentanedione or 2, 2, 6, 6-tetramethyl-3, 5-heptanedione.

thioether sulfoxides, thioether sulphones, optionally cyclic thioethers, di (thioethers), monoalcohols and polyols, dextrin and its derivatives, thiazolidines; hydrocarbon-based polymers optionally comprising hetero atoms chosen from N, O, S and P, said polymers, being obtained, for example, by free-radical polymerization, by condensation or by controlled "living" polymerization, and said polymers having a (weight-average) molecular weight ranging from 90 to 10 000, such as, for example, from 100 to 1 000, and as a further example from 150 to 500; and derivatives thereof.

[026] Mention may be made, for example, of:

- salicylic acid and its derivatives such as 4- (meth) - acrylaminosalicylic acid and 5-(meth) acrylamido-salicylic acid;
- lactic acid; succinic acid; acetic acid; citric acid;
- acrylic acid esters or methacrylic acid esters, such as acetoxyethyl (meth) acrylate; methyl  $\alpha$ - hydroxy (meth) acrylate;
- ethyl acetoacetate of formula  $\text{CH}_3\text{-CO-CH}_2\text{-COOCH}_2\text{CH}_3$ , methyl acetoacetate of formula  $\text{CH}_3\text{-CO-CH}_2\text{-COOCH}_3$  and acetylacetone of formula  $\text{CH}_3\text{-CO-CH}_2\text{-CO-CH}_3$ ;
- EDTA;
- low molecular weight polyethers (n ranging from 1 to 12) such as poly (ethylene glycols) and poly (propylene glycols);
- lysine and its derivatives, such as  $\epsilon$ -N- (meth) acryloyl-L-lysine;
- cysteine and its derivatives, such as N-acetylcysteine, N-acetylcysteine disulphides and carboxymethylcysteine;
- cystine; methionine;
- lactic acid esters or acetic acid esters
- triethanolamine;

[0065] For example, the at least one metallic precursor, according to the invention, is chosen from:

[0066] tetramethoxysilane, silicon, titanium or tin tetraethoxide; titanium, silicon or tin tetraisopropoxide; tin, titanium or silicon tetrabutoxide;

[0067] methyltriethoxysilane, methyltrimethoxysilane, mercaptopropyltriethoxysilane, 3-aminopropyl-triethoxysilane; allyltriethoxysilane;

[0068] N-triethoxysilylpropyl-N, N, N-tri-n-butylammonium chloride of formula  $(C_4H_9)_3N^+CH_2CH_2CH_2Si(OC_2H_5)_3, Cl^-$

[0069] N-triethoxysilylpropyl-N, N, N-tri-n-butylammonium bromide of formula  $(C_4H_9)_3N^+CH_2CH_2CH_2Si(OC_2H_5)_3, Br^-$

[0070] N— (trimethoxysilylpropyl) isothiuronium chloride of formula  $(NH_2)_2C=S^+CH_2CH_2CH_2Si(OCH_3)_3, Cl^-$

[0071] (3-glycidyloxypropyl) trimethoxysilane;

[0072] (3-(2-aminoethylamino) propyl) trimethoxysilane;

[0073] (3-(2-(2-aminoethylamino) ethylamino) propyl) trimethoxysilane;

[0074] (4-aminobutyl) triethoxysilane;

[0075] (N-(6-aminoethyl) aminopropyl) trimethoxysilane; *hyphen*

[0076] (N-methylamino)propyl) trimethoxysilane;

[0077] acetoxymethyltriethoxysilane;

[0078] 3-triethoxysilylpropylurea;

[0079] triethoxysilane

[0080] (3-aminopropyl) methyldiethoxysilane;

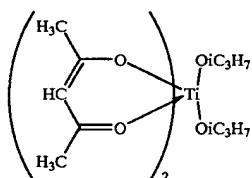
[0081] (mercaptomethyl) methyldiethoxysilane;

[0082] (3-mercaptopropyl) methyldimethoxysilane;

[0083] titanium diisopropoxide bis (triethanolamine) of formula  $[(HOCH_2CH_2)_2NCH_2CH_2O]_2Ti(OC_3H_7)_2$

[0084] methyldiethoxysilane, methyldimethoxysilane, allyldimethoxysilane;

[0085] titanium diisopropoxide bis (2, 4-pentanedionate) of formula:



[0086] zirconium diisopropoxide bis (2, 2, 6, 6-tetramethyl-3, 5-heptanedionate); and

[0087] bis (2, 4-pentanedionate) titanium-O, O'-bis(oxyethyl) aminopropyltriethoxysilane.

[0088] The at least one organometallic compound used in the context of the present invention may be obtained, for example, by partial or total hydrolysis, and partial or total condensation, of at least one metallic precursor as defined above, according to a well-known sol-gel process.

[0089] In general, but in a non-limiting manner, the at least one metallic precursor may initially be dissolved or dispersed in a co-solvent such as an oil of plant, mineral, organic or synthetic origin, such as those described below, and/or an alcohol, monoalcohol or polyol, for example, ethanol, such as those described below.

[0090] A hydrolysis reaction can then be carried out either by adding water or by means of the residual water, or by adding water "generators" (in which case the water will be generated in situ). A chelating compound may also optionally be introduced.

[0091] A sol of the desired at least one organometallic compound can thus be obtained, which may be in the form of colloidal particles suspended in the co-solvent, or in the form of a compound dissolved in the co-solvent. The colloidal particles are generally nanometer-sized, such as from about 0.2 to 100 nanometers, for example, from 0.5-50 nm and from 1-10 nm.

[0092] In the rest of the present description, the expression "organometallic compound sol" will mean the mixture of the organometallic compound and of its co-solvent.

[0093] For example, the organometallic compound sol has a solids content of 1-95% by weight, for example, 3-90% by weight and 4-60% by weight. The solids content is measured after heating the sol at 100° C. for 1 hour at ambient pressure (1 atm).

[0094] The co-solvent which may be used may be chosen from alcoholic solvents, such as  $C_{1-10}$  alcohols, such as methanol, ethanol, isopropanol, n-propanol, n-butanol, isobutanol, t-butanol, n-pentanol and hexanol; polyols such as propylene glycol, ethylene glycol, pentylene glycol, glycerol and sorbitol; and Miglyol®.

[0095] It is also possible to add 0-99.9% by weight water to the alcoholic solvent in order to obtain an aqueous-alcoholic mixture.

[0096] Co-solvents which may also be used include, for example:

[0097] ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone, diisobutyl ketone, isophorone and cyclohexanone;

[0098] glycol ethers, such as propylene glycol monomethyl ether, propylene glycol monomethyl ether acetate and dipropylene glycol aminobutyl ether;

[0099] aldehydes;

[0100] esters, such as acetates, for example butyl, propyl, ethyl, isopropyl, isopentyl and 2-methoxyethyl acetates, purcellin oil, and isopropyl myristate;

[0101] esters of mineral acid and of alcohol;

[0102] linear and branched, optionally aromatic, hydrocarbons, such as hexane, octane, hexadecane, heptanes, dodecane, cyclohexanone, liquid paraffin, xylene and



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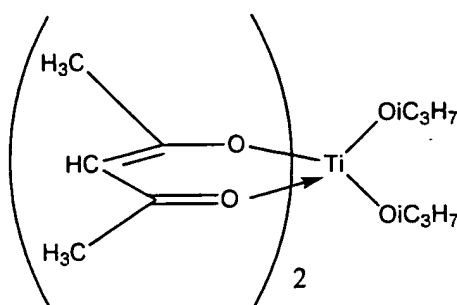
- cysteine and its derivatives;
- lipoic acids;
- dextrin and cyclodextrin;
- polymers of polyethylene glycol, polypropylene glycol or polyethyleneimine type; and
- diketones such as 2, 4-pentanedione, 2, 4- hexafluoropentanedione or 2, 2, 6, 6-tetramethyl-3, 5-heptanedione.

[027] For example, the at least one metallic precursor, according to the invention, is chosen from:

- tetramethoxysilane, silicon, titanium or tin tetraethoxide; titanium, silicon or tin tetraisopropoxide; tin, titanium or silicon tetrabutoxide;
- methyltriethoxysilane, methyltrimethoxysilane, mercaptopropyltriethoxysilane, 3-aminopropyl-triethoxysilane; allyltriethoxysilane;
- N-triethoxysilylpropyl -N, N, N-tri-n-butylammonium chloride of formula  $(C_4H_9)_3N^+CH_2CH_2CH_2Si(OC_2H_5)_3, Cl^-$
- N-triethoxysilylpropyl-N, N, N-tri-n-butylammonium bromide of formula  $(C_4H_9)_3N^+CH_2CH_2CH_2Si(OC_2H_5)_3, Br^-$
- N- (trimethoxysilylpropyl) isothiuronium chloride of formula  $(NH_2)_2C=S^+CH_2CH_2CH_2Si(OCH_3)_3, Cl^-$
- (3-glycidyloxypropyl) trimethoxysilane;
- (3-(2-aminoethylamino) propyl) trimethoxysilane;
- (3-(2-(2-aminoethylamino) ethylamino) propyl) trimethoxysilane;
- (4-aminobutyl) triethoxysilane;
- (N- (6-aminohexyl) aminopropyl) trimethoxysilane;
- (N-methylaminopropyl) trimethoxysilane;



- acetoxymethyltriethoxysilane;
- 3-triethoxysilylpropylurea;
- triethoxysilane
- (3-aminopropyl) methyldiethoxysilane;
- (mercaptomethyl) methyldiethoxysilane;
- (3-mercaptopropyl) methyldimethoxysilane;
- titanium diisopropoxide bis (triethanolamine) of formula  $[(\text{HOCH}_2\text{CH}_2)_2\text{NCH}_2\text{CH}_2\text{O}]_2\text{Ti}(\text{OC}_3\text{H}_7)_2$
- methyldiethoxysilane, methyldimethoxysilane, allyldimethoxysilane;
- titanium diisopropoxide bis (2, 4-pentanedionate) of formula:



- zirconium diisopropoxide bis (2, 2, 6, 6-tetramethyl-3, 5-heptanedionate); and
- bis (2, 4-pentanedionato) titanium-O, O' - bis (oxyethyl) aminopropyltriethoxysilane.

[028] The at least one organometallic compound used in the context of the present invention may be obtained, for example, by partial or total hydrolysis, and partial or total condensation, of at least one metallic precursor as defined above, according to a well-known sol-gel process.

[029] In general, but in a non-limiting manner, the at least one metallic precursor may initially be dissolved or dispersed in a co-solvent such as an oil of plant, mineral,

[0122] The keratin material which may be treated according to the invention may be chosen, for example, from the toenails, the fingernails, the eyelashes, the eyebrows, body hairs and head hair.

[0123] A composition according to the invention may thus be in the form of a make-up composition, such as a mascara or a treating mascara; a nail varnish, a varnish base or a nailcare product; a haircare composition, such as a styling lacquer, lotion or mousse, a styling spray or a styling stick.

#### EXAMPLE 1

[0124] Ethanol and water at pH 1 were introduced into a reactor equipped with a magnetic bar, a condenser and a dropping funnel. The mixture was placed under magnetic stirring for 15 minutes at 30° C. 10.4 g (0.05 mol) of tetraethoxysilane were added dropwise thereto with continued stirring for 48 hours. The reaction mixture was finally poured into a flask and placed at 30° C. The composition (or sol) thus obtained may be stored without further modification, so as to incorporate it subsequently into a cosmetic composition.

#### EXAMPLE 2

[0125] Ethanol and water at pH 1 were introduced into a reactor equipped with a magnetic bar, a condenser and a dropping funnel. The mixture was placed under magnetic stirring for 15 minutes at 30° C. 11 g (0.05 mol) of aminopropyltriethoxysilane were added dropwise thereto and vigorous stirring was maintained for 48 hours. The reaction mixture was finally poured into a flask and placed at 30° C. The composition thus obtained was stored without further modification, so as to incorporate it subsequently into a cosmetic composition.

#### EXAMPLE 3

[0126] Ethanol and water at pH 1 were introduced into a reactor equipped with a magnetic bar, a condenser and a dropping funnel. The mixture was placed under magnetic stirring for 15 minutes at 30° C. 8.9 g (0.05 mol) of methyltriethoxysilane were added dropwise thereto and vigorous stirring was maintained for 48 hours. The reaction mixture was finally poured into a flask and placed at 30° C. The composition thus obtained was stored without further modification, so as to incorporate it subsequently into a cosmetic composition.

#### EXAMPLE 4

[0127] A dynamic flexural characterization was carried out on nails treated with the compositions of Examples 2 and 3 and with a comparative commercial hardening composition "Durcilon" from Gemey.

[0128] The dynamic flexural characterization made it possible to determine the viscoelastic properties of a material in terms of elasticity and viscosity.

[0129] It consists in imposing a repeated sinusoidal stress (displacement) of small amplitude  $\Delta l$  on a sample. The sample reacted to the stress by opposing a sinusoidal force of amplitude  $\Delta F$ , which was phase-shifted relative to the stress by an angle  $\delta$ .

[0130] The viscoelastic nature of the material may be characterized by the modulus of stiffness  $K$  (N/m) which

corresponds to the overall rigidity of the sample, as may be determined by pulling or crushing the sample; and by the loss of angle  $\delta$  (in degrees) which characterizes the intrinsic viscosity. The greater the loss angle, the greater the viscosity of the material and the more delayed the material's response of the material and the more delayed the material's response to the stress.

$$\delta \propto \eta'$$

$$K(N/m) = \frac{\Delta F}{\Delta l}$$

[0131] Samples of natural human nails were cut with scissors into the shape of a 4 mm×5 mm rectangle.

[0132] Before any measurement, they were left for 48 hours in a glove box at a temperature of 25° C. and under a relative humidity of 45%.

[0133] 3 drops of the compositions prepared in Example 2 and 3 were applied to the samples using a micropipette.

[0134] The treated samples were then left for 24 hours in a glove box at a temperature of 25° C. and under relative humidity of 45%, in order for the solvent to evaporate completely.

[0135] For each of the samples, the value of the modulus of stiffness  $K$  and the loss angle  $\delta$  was determined before and after treatment.

[0136] A Metravib VA 2000 viscoelasticimeter was used, which allows measurements to be taken directly in the glove box ( $T=25^\circ\text{C}$ ;  $R.H.=45\%$ ).

[0137] The sample was gripped in fixing jaws via the "root side" of the end of the nail. The dynamic measuring head of the viscoelasticimeter repeatedly stresses the free end (opposite edge) of the nail by means of a knife. A constant (flexural) deformation, on which was superimposed a sinusoidal stress-the wave flexure-was applied to the nail. The nail remained overall always flexed in the same direction.

[0138] The conditions were as follows:

[0139] static displacement:  $d_{\text{stat}}=-300\text{ }\mu\text{m}$  approximately, which corresponds to a static force  $F$  of

[0140] 0.6 N

[0141] amplitude of the dynamic displacements:  $d_{\text{dyn}}=\pm 30\text{ }\mu\text{m}$  approximately

[0142] sinusoidal stress frequency:  $f=10\text{ Hz}$

[0143] The value of  $\Delta F$ , and thus of  $K$ , and of  $\delta$ , were determined before treatment, after 1 day and after 7 days of treatment. The values of  $\Delta K$  and of  $\Delta\delta$  were deduced therefrom, after 1 and 7 days.

$$\Delta K(\%) = \frac{K_{\text{after}} - K_{\text{before}}}{K_{\text{before}}} \times 100$$

$$\Delta\delta(\%) = \frac{\delta_{\text{after}} - \delta_{\text{before}}}{\delta_{\text{before}}} \times 100$$

#### **Example 4**

[054] A dynamic flexural characterization was carried out on nails treated with the compositions of Examples 2 and 3 and with a comparative commercial hardening composition "Durcilog" from Gemey.

[055] The dynamic flexural characterization made it possible to determine the viscoelastic properties of a material in terms of elasticity and viscosity.

[056] It consists in imposing a repeated sinusoidal stress (displacement) of small amplitude  $\Delta l$  on a sample. The sample reacted to the stress by opposing a sinusoidal force of amplitude  $\Delta F$ , which was phase-shifted relative to the stress by an angle  $\delta$ .

[057] The viscoelastic nature of the material may be characterized by the modulus of stiffness  $K$  (N/m) which corresponds to the overall rigidity of the sample, as may be determined by pulling or crushing the sample; and by the loss of angle  $\delta$  (in degrees) which characterizes the intrinsic viscosity. The greater the loss angle, the greater the viscosity of the material and the more delayed the material's response of the material and the more delayed the material's response to the stress.

$$K \text{ (N/m)} = \frac{\Delta F}{\Delta l}$$

[058] Samples of natural human nails were cut with scissors into the shape of a 4 mm x 5 mm rectangle.

[059] Before any measurement, they were left for 48 hours in a glove box at a temperature of 25°C and under a relative humidity of 45%.

[060] 3 drops of the compositions prepared in Example 2 and 3 were applied to the samples using a micropipette.

[0144] The following result were obtained:

	K before treatment (N/m)	K after 1 day (N/M)	K After 7 days (N/m)	$\Delta K$ (1 day)	$\Delta K$ (7 days)	$\delta$ before treatment	$\delta$ after 1 day	$\delta$ After 7 days	$\Delta\delta$ (1 day)	$\Delta\delta$ (7 days)
Example 2 (solids content 10.2%)	6830	7770	8090	13.76	18.45	2.9	4.2	4.0	44.83	37.93
Example 3 (solids content 5.9%)	6930	7490	7770	8.08	12.12	2.8	3.2	3.4	14.29	21.43
Durcilon <sup>®</sup> (solids content 13%)	8770	9910	10300	13.00	17.44	3.3	6.5	6.1	96.97	84.85

[0145] It was thus found that the compounds of Examples 2 and 3 gave results that were comparable, in terms of rigidification, with those obtained with a commercial nail-strengthening product, for lower solids contents.

#### EXAMPLE 5

[0146] Vickers hardness measurements were carried out on nails treated with the composition Example 2 above.

[0147] The measurement was carried out in the following way:

[0148] Nails samples were collected from several donors. They were cut into small rectangles 2 to 3 mm wide in the median longitudinal part and 3 to 4 mm long approximately.

[0149] Three fragments were bonded to a rectangular stainless steel support using an adhesive of "cyanolite" type. 3 plots were prepared per product, i.e. 9 fragments. The samples were then conditioned at a relative humidity of 75% and at a temperature of 30° C., for 48 hours.

[0150] A first measurement was carried out on the untreated samples.

[0151] Next, 0.5  $\mu$ l per mm<sup>2</sup> of the test composition was applied to each nail fragment. The fragments were then conditioned at a relative humidity of 75% and at a temperature of 30° C. for 48 hours.

[0152] The Vickers hardness coefficient (VH) was determined using an M 400 G2 Leco<sup>®</sup> microdurometer, with the following conditions:

[0153] application load: 50 gf

[0154] application time: 15 sec

[0155] application speed: 60  $\mu$ m/sec

[0156] The following results were obtained:

	Vickers hardness (VH)
Untreated Nails	16
Nails treated with the composition of Example 2	18

[0157] An increased of about 12.5% in the hardness of the nails treated with the composition according to the invention was thus observed.

#### EXAMPLE 6

[0158] A composition was prepared comprising, on a weight basis:

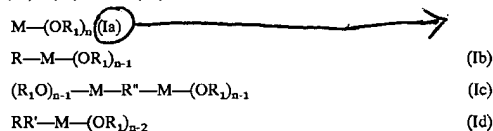
thickener	2%
colorant	0.2%
preserving agent, fragrance	Qs
composition of Example 1	qs 100%

[0159] A composition which may be applied to the nails was obtained.

What is claimed is:

1. A method of protecting and/or strengthening a keratin material comprising applying to said keratin material an effective amount of a composition comprising at least one organometallic compound obtained from at least one metallic precursor chosen from:

(a) at least one metal alkoxide chosen from formulae (Ia), (Ib), (Ic), and (Id) below:



wherein:

M and M', which may be identical or different, denote a metal atom chosen from the transition metals of groups Ib to VIIb of the Periodic Table, group VIII of the Periodic Table, the lanthanide group of the Periodic Table, aluminum, silicon, boron, tin, magnesium, alkali metals and alkaline-earth metals;

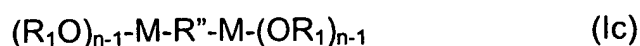
n denotes the valency of the metal;

R<sub>1</sub>, which may be identical or different, is chosen from linear and branched, saturated and unsaturated hydrocarbon-based radicals containing 1 to 30 carbon atoms,

**WHAT IS CLAIMED IS:**

1. A method of protecting and/or strengthening a keratin material comprising applying to said keratin material an effective amount of a composition comprising at least one organometallic compound obtained from at least one metallic precursor chosen from:

(a) at least one metal alkoxide chosen from formulae (la), (lb), (lc), and (ld) below:



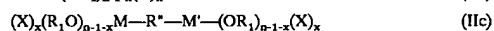
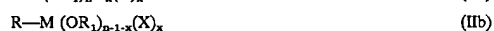
wherein:

- M and M', which may be identical or different, denote a metal atom chosen from the transition metals of groups Ib to VIIb of the Periodic Table, group VIII of the Periodic Table, the lanthanide group of the Periodic Table, aluminum, silicon, boron, tin, magnesium, alkali metals and alkaline-earth metals;
- n denotes the valency of the metal;
- R<sub>1</sub>, which may be identical or different, is chosen from linear and branched, saturated and unsaturated hydrocarbon-based radicals containing 1 to 30 carbon atoms,
- R and R', which may be identical or different, are chosen from hydrogen, linear, branched and cyclic, saturated and unsaturated, C<sub>1-30</sub> hydrocarbon-based radicals, and a cosmetically active group; and
- R'' is chosen from -O-, -NR<sup>2</sup>-, -S-, linear, cyclic and branched, saturated and unsaturated, C<sub>1-30</sub> divalent hydrocarbon-based radicals, and a cosmetically active group, wherein R<sup>2</sup> is chosen from linear, cyclic and branched, saturated and unsaturated C<sub>1-30</sub> hydrocarbon-based radicals;

R and R', which may be identical or different, are chosen from hydrogen, linear, branched and cyclic, saturated and unsaturated, C<sub>1-30</sub> hydrocarbon-based radicals, and a cosmetically active group; and

R" is chosen from —O—, —NR<sup>2</sup>—, —S—, linear, cyclic and branched, saturated and unsaturated, C<sub>1-30</sub> divalent hydrocarbon-based radicals, and a cosmetically active group, wherein R<sup>2</sup> is chosen from linear, cyclic and branched, saturated and unsaturated C<sub>1-30</sub> hydrocarbon-based radicals;

(b) at least one complex chosen from formulae (IIa), (IIb), (IIc) and (IId) below:



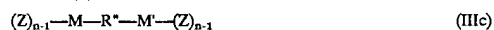
wherein:

M, M', n, R, R', R" and R<sub>1</sub> have the same meaning as above;

X is a ligand comprising an atom chosen from nitrogen, phosphorus, sulphur and oxygen; and

x is the number of atoms which may link to the central metal atom;

(c) at least one metal halide chosen from formulae (IIIa), (IIIb), (IIIc) and (IIId) below:

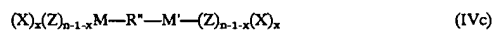


wherein:

M, M', n, R, R' and R" have the same meaning as above; and

Z, which may be identical or different, is chosen from a halogen atom; and

(d) at least one complexes chosen from formulae (IVa), (IVb), (IVc) and (IVd) below:



wherein:

M, M', n, R, R', R", X, x and Z have the same meaning as above; and

wherein said cosmetically active group is chosen from a colorant group; a photochromic group; a group for screening out UV-A and/or UV-B radiation; a group for promoting adhesion to keratin materials, such as an amide, urethane, urea, hydroxyl, carboxyl, amino acid or polypeptide group; a group which facilitates make-up removal; a bacterial or bacteriostatic group; a chelating group, for example, one which can complex multivalent cations; a hydroxy acid; a group for preventing hair loss; an antioxidant group; a free-radical-scavenging group; and a vitamin-bearing group.

2. A method according to claim 1, wherein said at least one organometallic compound is obtained by at least one of partial and total hydrolysis of said at least one metallic precursor and partial and total condensation of said at least one metallic precursor.

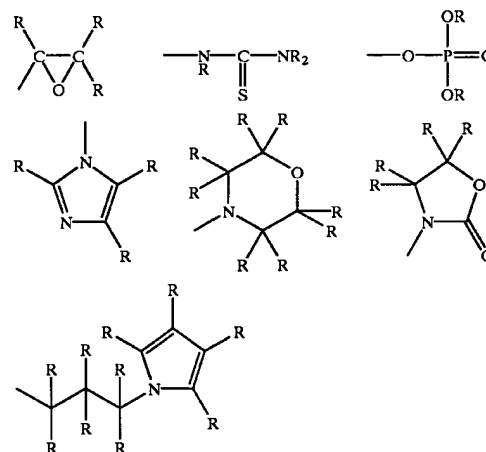
3. A method according to claim 1, wherein R<sub>1</sub> is chosen from linear and branched, saturated and unsaturated hydrocarbon-based radicals containing 1 to 6 carbon atoms, optionally interrupted by and/or substituted with 1-20 hetero atoms chosen from O, N, S and P.

4. A method according to claim 1, wherein R and R', which may be identical or different, are chosen from hydrogen, linear, branched and cyclic, saturated and unsaturated C<sub>2-20</sub> hydrocarbon-based radicals, optionally substituted and/or interrupted with 1-20 hetero atoms chosen from O, N, S and P.

5. A method according to claim 1, wherein R" is chosen from linear, cyclic and branched, saturated and unsaturated, C<sub>2-20</sub> divalent hydrocarbon-based radicals, optionally interrupted and/or substituted with 1-20 hetero atoms chosen from O, N, P and/or S.

6. A method according to claim 1, wherein R<sup>2</sup> is chosen from linear, cyclic and branched, saturated and unsaturated C<sub>2-20</sub> hydrocarbon-based radicals.

7. A method according to claim 1, wherein at least one of R, R', and R", which may be identical or different, are substituted with at least one substituent chosen from a halogen atom, —NR<sub>2</sub>, —CO—NR<sub>2</sub>, —SR, —R—S—R, —CO<sub>2</sub>R, —COR, —OH, —N=C=O, —NR—CO—NR<sub>2</sub>, —N<sup>+</sup>R<sub>3</sub>, —S<sup>+</sup>=C(NR<sub>2</sub>)<sub>2</sub>; sulphonate (—SO<sub>3</sub>R);



wherein R, which may be identical or different, are chosen from hydrogen and linear, branched and cyclic, saturated and unsaturated, C<sub>1-30</sub> hydrocarbon-based radicals.

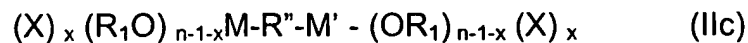
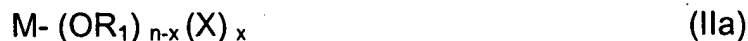
8. A method according to claim 1, wherein said ligand optionally bears at least one cosmetically active group.

9. A method according to claim 1, wherein Z is chosen from chlorine, iodine, bromine and fluorine.

10. A method according to claim 1, wherein said amount is effective to at least one of quickly and durably improve the rigidity of said keratin material and quickly and durably improve cohesion of said keratin material.

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(b) at least one complex chosen from formulae (IIa), (IIb), (IIc) and (IIId) below:



wherein:

- M, M', n, R, R', R'' and R<sub>1</sub> have the same meaning as above;
- X is a ligand comprising an atom chosen from nitrogen, phosphorus, sulphur and oxygen;
- and
- x is the number of atoms which may link to the central metal atom;

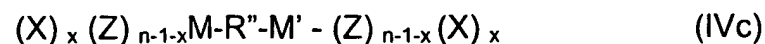
(c) at least one metal halide chosen from formulae (IIIa), (IIIb), (IIIc) and (IIId) below:



wherein:

- M, M', n, R, R' and R'' have the same meaning as above; and
- Z, which may be identical or different, is chosen from a halogen atom; and

(d) at least one complexes chosen from formulae (IVa), (IVb), (IVc) and (IVd) below:



wherein:

37. A method according to claim 36, wherein said hydrocarbon-based polymers have a weight-average molecular weight ranging from 150 to 500.

38. A method according to claim 1, wherein said at least one metallic precursor is chosen from:

tetramethoxysilane, silicon tetraethoxide, titanium tetraethoxide, tin tetraethoxide; titanium tetraisopropoxide, silicon tetraisopropoxide, tin tetraisopropoxide; tin tetrabutoxide, titanium tetrabutoxide, silicon tetrabutoxide;

methyltriethoxysilane, methyltrimethoxysilane, mercaptopropyltriethoxysilane, 3-aminopropyl-triethoxysilane; allyltriethoxysilane;

N-triethoxysilylpropyl-N, N, N-tri-n-butylammonium chloride of formula  $(C_4H_9)_3N^+CH_2CH_2CH_2Si(OC_2H_5)_3, Cl^-$

hyphen N-triethoxysilylpropyl-N, N, N-tri-n-butylammonium bromide of formula  $(C_4H_9)_3N^+CH_2CH_2CH_2Si(OC_2H_5)_3, Br^-$

N-(trimethoxysilylpropyl) isothiuronium chloride of formula  $(NH_2)_2C=S^+CH_2CH_2CH_2Si(OCH_3)_3, Cl^-$

(3-glycidyloxypropyl) trimethoxysilane;

(3-(2-aminoethylamino) propyl) trimethoxysilane;

(3-(2-(2-aminoethylamino) ethylamino) propyl) trimethoxysilane;

(4-aminobutyl) triethoxysilane;

(N-(6-aminohexyl) aminopropyl) trimethoxysilane;

(N-methylaminopropyl) trimethoxysilane;

acetoxymethyltriethoxysilane;

3-triethoxysilylpropylurea;

triethoxysilane

(3-aminopropyl) methyltriethoxysilane;

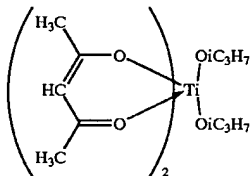
(mercaptomethyl) methyltriethoxysilane;

(3-mercaptopropyl) methyltrimethoxysilane;

titanium diisopropoxide bis (triethanolamine) of formula  $[(HOCH_2CH_2)_2NCH_2CH_2O]_2Ti(OC_3H_7)_2$

methyltriethoxysilane, methyltrimethoxysilane, allyltrimethoxysilane;

titanium diisopropoxide bis (2, 4-pentanedionate) of formula:



zirconium diisopropoxide bis (2, 2, 6, 6-tetramethyl-3, 5-heptanedionate); and

bis (2, 4-pentanedionate) titanium-O, O'-bis (oxyethyl) aminopropyltriethoxysilane.

39. A method according to claim 1, wherein said composition comprises a sol of said at least one organometallic compound.

40. A method according to claim 39, wherein said composition comprises 1% to 100% by weight of said organometallic compound sol.

41. A method according to claim 39, wherein said composition comprises 1.5% to 95% by weight of said organometallic compound sol.

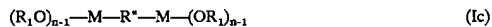
42. A method according to claim 39, wherein said composition comprises 10% to 90% by weight of said organometallic compound sol.

43. A method according to claim 39, wherein said composition comprises 12% to 50% by weight of said organometallic compound sol.

44. A method of protecting and/or strengthening a keratin material comprising applying to said keratin material an effective amount of a composition comprising at least one organometallic compound.

45. A composition in the form of a make-up composition, a nail varnish, a varnish base, a nail-care product or a hair-care product, said composition comprising at least one organometallic compound obtained from at least one metallic precursor chosen from:

(a) at least one metal alkoxide chosen from formulae (Ia), (Ib), (Ic), and (Id) below:



wherein:

M and M', which may be identical or different, denote a metal atom chosen from the transition metals of groups Ib to VIIb of the Periodic Table, group VIII of the Periodic Table, the lanthanide group of the Periodic Table, aluminum, silicon, boron, tin, magnesium, alkali metals and alkaline-earth metals;

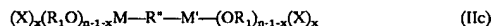
n denotes the valency of the metal;

R<sub>1</sub>, which may be identical or different, is chosen from linear and branched, saturated and unsaturated hydrocarbon-based radicals containing 1 to 30 carbon atoms,

R and R', which may be identical or different, are chosen from hydrogen, linear, branched and cyclic, saturated and unsaturated, C<sub>1-30</sub> hydrocarbon-based radicals, and a cosmetically active group; and

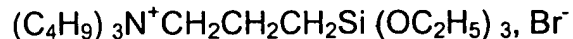
R'' is chosen from —O—, —NR<sup>2</sup>—, —S—, linear, cyclic and branched, saturated and unsaturated, C<sub>1-30</sub> divalent hydrocarbon-based radicals, and a cosmetically active group, wherein R<sup>2</sup> is chosen from linear, cyclic and branched, saturated and unsaturated C<sub>1-30</sub> hydrocarbon-based radicals;

(b) at least one complex chosen from formulae (IIa), (IIb), (IIc) and (IId) below:

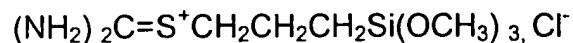




- N-triethoxysilylpropyl-N, N, N-tri-n-butylammonium bromide of formula



- N- (trimethoxysilylpropyl) isothiuronium chloride of formula



- (3-glycidyloxypropyl) trimethoxysilane;

- (3-(2-aminoethylamino) propyl) trimethoxysilane;

- (3-(2-(2-aminoethylamino) ethylamino) propyl) trimethoxysilane;

- (4-aminobutyl) triethoxysilane;

- (N- (6-aminoethyl) aminopropyl) trimethoxysilane;

- (N-methylaminopropyl) trimethoxysilane;

- acetoxymethyltriethoxysilane;

- 3-triethoxysilylpropylurea;

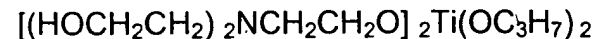
- triethoxysilane

- (3-aminopropyl) methyldiethoxysilane;

- (mercaptomethyl) methyldiethoxysilane;

- (3-mercaptopropyl) methyldimethoxysilane;

- titanium diisopropoxide bis (triethanolamine) of formula



- methyldiethoxysilane, methyldimethoxysilane, allyldimethoxysilane;

- titanium diisopropoxide bis (2, 4-pentanedionate) of formula: